CO_2: ADSORPTION ON PALAGONITE AND THE MARTIAN REGOLITH

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If there was ever sufficient CO_2 in the martian atmosphere to engender a greenhouse effect sufficient to raise the surface temperature above 273 K, most of that CO_2 is missing today.

Pollack et al., (1986) calculated that, even if reduced solar luminosity is accounted for, 0.75 bars of CO_2 could have provided surface temperatures greater than 273K at restricted times and places. We consider 0.75 bars to be the lower limit on the early atmospheric CO_2 abundance necessary for a greenhouse effect.

Known reservoirs of CO_2 do not hold anywhere near 0.75 bars. Only 8 mbar is currently in the atmosphere, less than 10 mb has escaped to space (Pollack and Yung, 1980), and no more than a few mbar are in the permanent south polar cap reservoir (Fanale et al., 1982). In the absence of a deep subsuction mechanism, the remainder must have been lost to space, or be stored in the regolith, either as carbonate rock or in the adsorbed state.

Based on laboratory measurements of CO_2 adsorption on basalt and nontronite, (Fanale et al., 1982), suggested that it is unlikely that the regolith could have adsorbed more than about 0.28 bars of CO_2.

The possible scenarios for the evolution of the martian climate are likely to lie along a continuum whose end members may be defined as follows:

1) The abundant erosional features indeed indicate the presence of fresh liquid water (eutectic = 273K) on the martian surface. That water was stablized by the presence of a massive CO_2 atmosphere, at least 0.4 bars of which cannot be accounted for in known reservoirs, and which presumably exists as carbonate in the regolith.

2) The erosional activity was accomplished mainly by Martian brines (Brass, 1980) with depressed eutectics. In this case, sapping, and not rainfall is involved, and the difficulties associated with fresh water erosion are mitigated, but not removed. A greenhouse may still be required, but less than 0.75 bars would be necessary, and it may be that the entire CO_2 inventory necessary for a greenhouse effect of the required magnitude could be accommodated today in the adsorbed state without recourse to carbonates.

In the interest of determining an upper limit on the adsorptive capacity of the martian regolith, we recently examined the results of Fanale and Cannon, (1971,1974) for CO_2 adsorption on nontronite and basalt. There appeared to be a strong proportionality between the capacity of the adsorbent and its specific surface area. In order to investigate the hypothesis that the specific surface area of the adsorbent could be used to constrain its adsorptive capacity, even in the absence of mineralogical information, we performed additional adsorption measurements of CO_2 on palagonites from Mauna Kea, Hawaii. We chose palagonites because they are a weathering product of basaltic glass and form a good spectral and chemical analog to the Viking soils (Evans and Adams, 1980, Singer, 1982). Weathering products generally dominate adsorption behavior, and nontronite is now in disfavor as a Mars analog material because of features in its spectrum which are undetectable or absent in Mars' spectrum.

Determining the relative importance of surface area and mineralogy is important becasue *in situ* measurements of specific surface area for Martian materials

exist, whereas no determination of mineralogy has ever been made.

Adsorption measurements were made on a Micrometrics AccuSorb 2100E Physical Adsorption Analyzer. We found that our data were reproducible to approximately 40% at low adsorptive coverage, but that precision increased to better than 20% at higher coverage. The desorption branches of the isotherms were reproducible, provided the preceding adsorption branches were carried up to near saturation. Unfortunately, the high saturation pressure of CO_2 complicated this in higher temperature data runs. However, the BET surface area, which we calculated for each isotherm, provides another check on internal consistency. Performing a least-squares fit on the data, we find that the data can be fitted to a curve of the form

$$\rho_a = \delta\, P^\gamma\, T^\beta \tag{1}$$

where $\delta = 27.93$, $\gamma = 0.171045$, and $\beta = -1.44675$. Here P is in mm Hg, and T is degrees Kelvin. The associated error in this equation is $\pm 20\%$, based on the spread in the data.

Normalizing for the surface area of all three minerals, decreases the uncertainty associated with not knowing the composition of the adsorbent to less than a factor of three from approximately a factor of 13. We believe that accounting for specific surface area provides a significant improvement in our estimate of the capacity of a mafic particulate adsorbent at Mars-like conditions. More importantly, it provides a description of the response to temperature variation which is less mineralogy-dependent and more useful in predicting climate change than those used in the past.

For the purposes of this study, we therefore assume that an equation can be written which describes CO_2 adsorption on any basalt or basaltic weathering product in terms of temperature, P_{CO_2} and the specific surface area of the material, without regard to mineralogy. We do not apply this equation to temperature and pressure conditions which differ from the conditions at which the data were gathered. The complete data set for all minerals was used to fit that equation. The equation which best describes the general CO_2 adsorptive behavior of particulate mafic rocks and their weathering products is

$$\rho_a = A_s\, \delta\, P^\gamma T^\beta \tag{2}$$

Where A_s is the specific surface area of the material in $(m^2\, g^{-1})$, and P and T are as above. In this case $\delta = 5.9629 \times 10^4$, $\gamma = 0.364391$, and $\beta = -3.83415$. A check of this equation indicates that it predicts adsorptive capacity to within a factor of three for those mafic rocks and weathering products for which CO_2 adsorption data are available, regardless of precise mineralogy.

If we are granted the indulgence of scooping up a few cubic centimeters of soil and extrapolating to the entire unconsolidated regolith, we can use Eq.(2) to draw some constraints on the partitioning of CO_2 in the martian regolith.

Fanale et al. (1982) presented a model of the martian climate in which they considered regolith adsorption to be the primary reservoir of exchangeable CO_2. They presented results based on basalt and nontronite, and described cap formation and atmospheric pressure as a function of obliquity. We have reconfigured that model, eliminating explicit assumptions of mineralogy, and substituting Eq.(2) with $A_s = 17\, m^2\, g^{-1}$.

There are two independent variables in the current configuration of this model. One is the amount of *exchangeable* CO_2, (i.e. adsorbed, atmospheric, or cap CO_2). The other variable is the depth of the regolith, which essentially determines the total surface area available for adsorption. This model is useful because if we specify the depth of the regolith that is in diffusive contact with the atmosphere, then there is a unique amount of exchangeable CO_2 that is compatible with, 1) the current atmospheric pressure, and 2) the absence of a significant current polar CO_2 reservoir. Our model allows us to find that amount of exchangeable CO_2.

The depth of the regolith in our model is not the depth of crustal fracturing, but a conceptual construct. It is the equivalent depth of a model regolith, with specific surface area $17 \, m^2 \, g^{-1}$, in diffusive contact with the atmosphere. A relatively small thickness of this idealized regolith would be the equivalent, in terms of total surface area, of a rather extensive real regolith, with sills, blocks, adsorbed H_2O and probably extensive permafrost. Our model indicates that even 500m of this ideal, highly adsorptive regolith could hold no more than 0.19 bars.

There are reasons to place a lower limit on regolith thickness as well. If we fix the total amount of outgassed CO_2, and make the regolith progressively shallower, the concentration of carbonate in the regolith must increase, assuming that CO_2 displaced from adsorbate would remain in the regolith. Eventually, a finite amount of carbonate should be present at the surface. Nonetheless, there is no spectral evidence for the existence of carbonates on Mars. That argues against a massive carbonate deposit of unconstrained mass as a panacea for models involving massive greenhouse effects early in martian history. Nonetheless, it is clear that some reservoir over and above adsorbate is almost certainly necessary.

This model allows us to make some estimates of exchangeable CO_2 abundances without knowing much more than we do now about martian volatile history. All atmospheric pressure vs. obliquity curves cross at obliquity 25° and pressure 7.5 mbar, as would be expected since the pairs of independent variables were chosen to be consistent with current conditions. However as long as the exchangeable CO_2 abundance and regolith depth are chosen with those constraints in mind, atmospheric pressure and cap formation as a function of obliquity is only weakly dependent on the specific parameters we chose. The actual mass of the polar cap at low obliquity of course does depend strongly on total exchangeable CO_2, but the atmospheric pressure does not at any obliquity.

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